Tagging Carbon Dioxide to Enable Quantitative Inventories of Geological Carbon Storage

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Outline

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- Research Objectives and Goal
- Radiocarbon (^{14}C) as an Inventory Tool
- Approach & Activities
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DOE/NETL Goals For MVA

Year	Goal
2008	Develop MVA protocols that enable recognition of leakage to the atmosphere and shallow subsurface in order to ensure 95 percent retention of stored CO_2.
2012	Develop MVA protocols that enable recognition of leakage to the atmosphere and shallow subsurface in order to ensure 99 percent retention of stored CO_2.

Source: NETL (2009). Monitoring, verification and accounting of CO_2 stored in deep geologic formations. Best Practice Manual, DOE/NETL-311/081508.

CO_2 Inventory

$$CO_2 \text{ stored} = \Sigma CO_2 \text{ injected} - \Sigma CO_2 \text{ leakage}$$

Motivation & Relevance

Public acceptance will require accurate monitoring and accounting of CO_2

- Commercial CO_2 geological storage projects are coming on line.
- Inventory of stored CO_2 will be required for accounting purposes.
- Conventional geophysical and geochemical MVA technologies are qualitative to semi-quantitative.
- **Mass-balance and dissolution/mineral trapping monitoring need new MVA tools**
- Long-term monitoring requires new geochemical MVA tools

Research Objectives and Goal

Develop a ^{14}C inventory technology for quantitative monitoring of CO_2 storage

- Develop an injection system for tagging large streams of CO_2 with ^{14}C
- Design and construct two alternative tracer injection systems, one for pure gases ($^{14}CO_2$, SF_6), and one for tracer gases dissolved in liquid.
- Design and develop an improved ^{14}C counting device.
- Field test of the ^{14}C tagging system.

^{14}C as an Inventory Tracer

Carbon Isotopes

Stable: ^{12}C - 98.93%

^{13}C - 1.07% $^{13}C/^{12}C = 0.01$

Radioactive: $\mathbf{^{14}C}$ **1ppt** $\mathbf{^{14}C/^{12}C = 1.3 \times 10^{-12}}$ (pre-industrial)

half-life of about 5730 years

decays by 0.158 MeV β^- emission

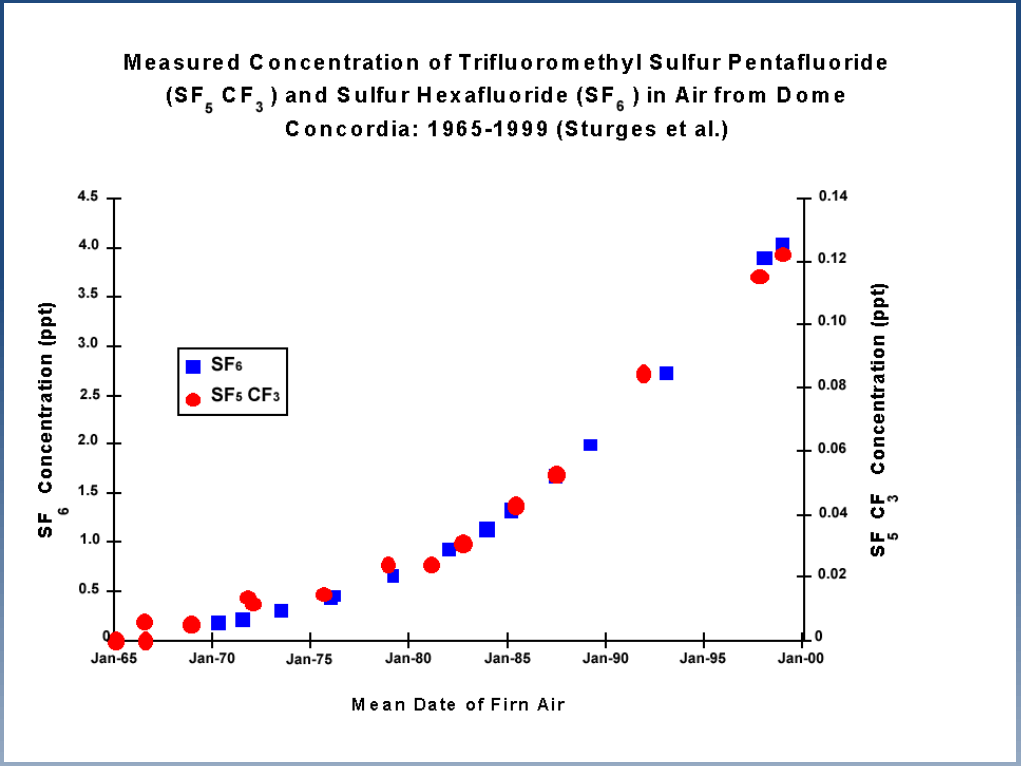
natural production in atmosphere is 38,000 Ci/year

- deep reservoirs have no or very small amounts of ^{14}C
- ^{14}C as a smart tracer for:
  - reaction processes (dissolution – precipitation)
  - biogeochemical processes
  - mixing processes in combination with conservative tracers
  - inventory of stored CO_2

^{14}C as an Inventory Tracer

- A storage reservoir that takes 1000 kg/sec of CO_2 would require a daily dose of 0.09 gram of $^{14}CO_2$ with an activity of 123 mCi.
- The annual production of ^{14}C in nuclear power plants and DOE facilities is around 600 Ci/year (Argonne, 2007).
- ^{14}C-accounting will require sampling the reservoir for liquids, gases and ideally solid core samples.
- The number of samples that need to be taken can be kept small if sampling augments other subsurface monitoring technologies (e.g. 3-D seismic, VSP, time lapse gravity etc.).

Sulfur Hexafluoride (SF_6)

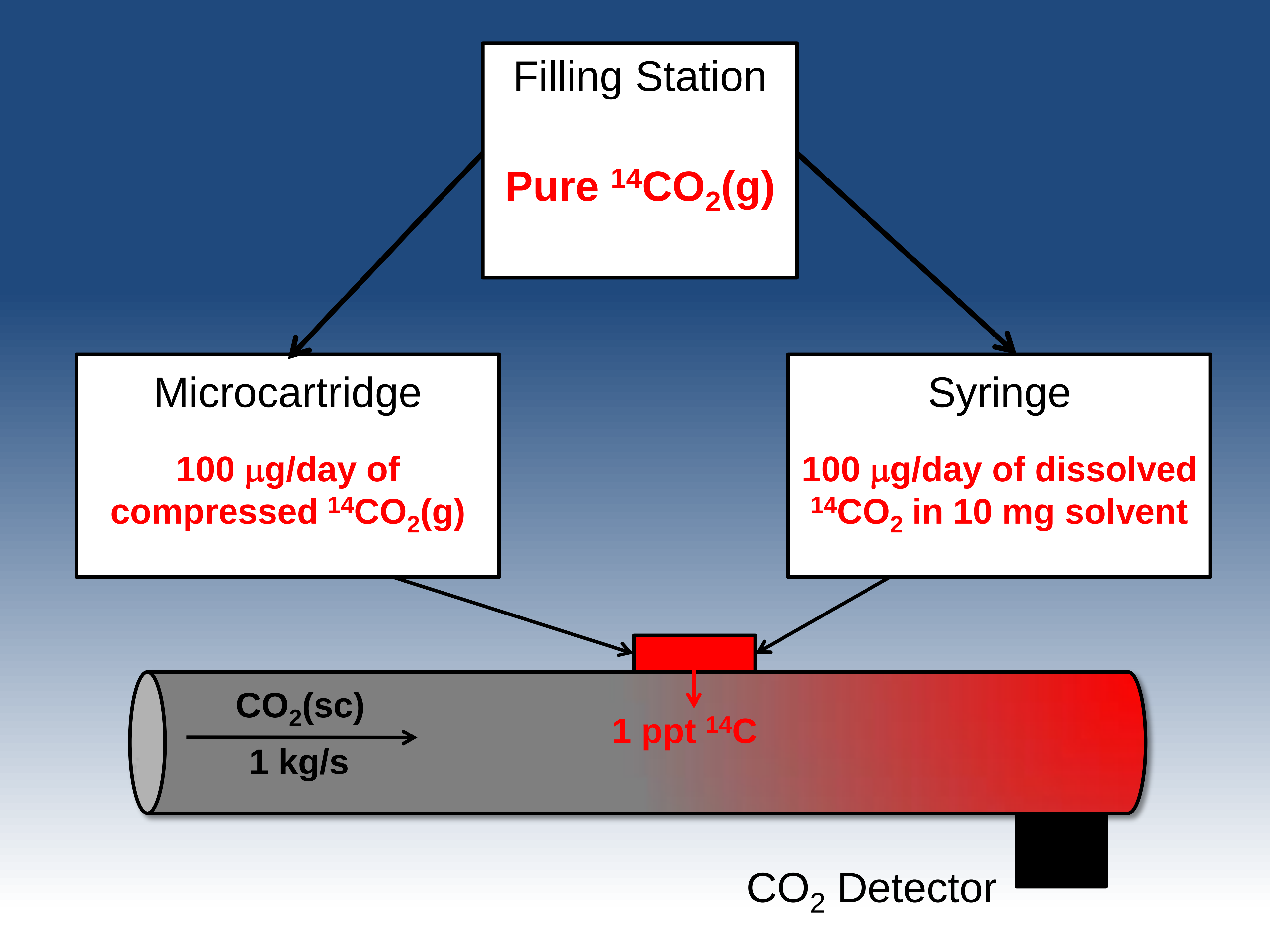


http://cdiac.ornl.gov/trends/otheratg/sturges/sturges.gif

- Used as a conservative (inert) tracer to track transport of injected fluids and detect leaks in adjacent formations.
- Used in our system as a non-radioactive substitute for testing equipment.
- Can be measured fairly easily in gas or aqueous samples in the sub-ppt concentration range with gas chromatography.

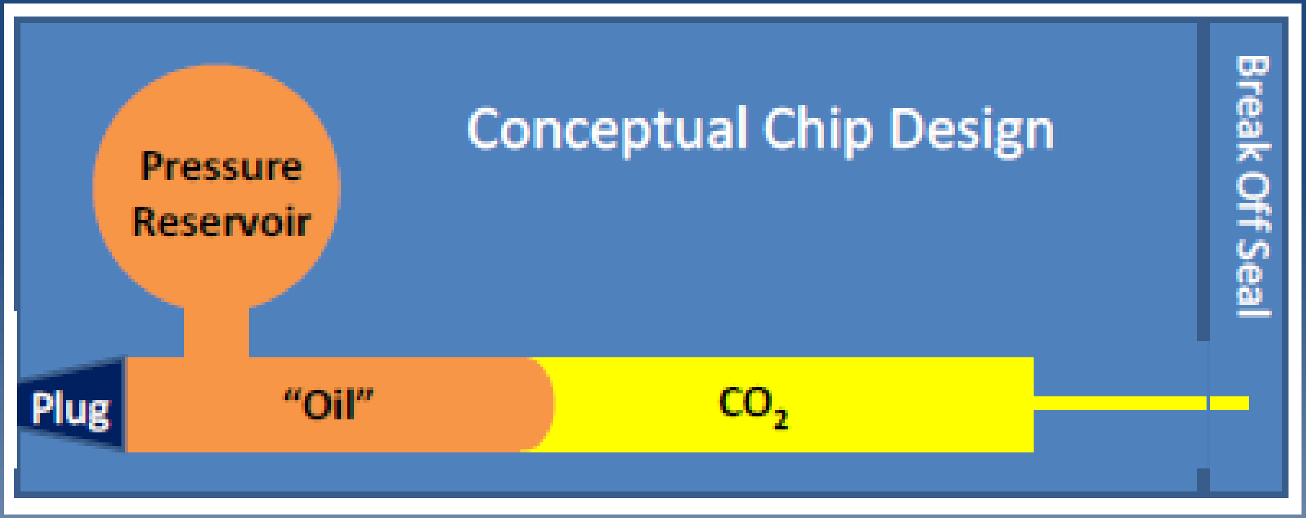
Design and Performance Requirements

- Tagging of 1Gt CO_2 requires 320 grams of ^{14}C
- Injection of 1 ppt of ^{14}C into a 1 kg/s of CO_2 flux (atmospheric concentration)
- ^{14}C supply units are designed for 1 day of supply



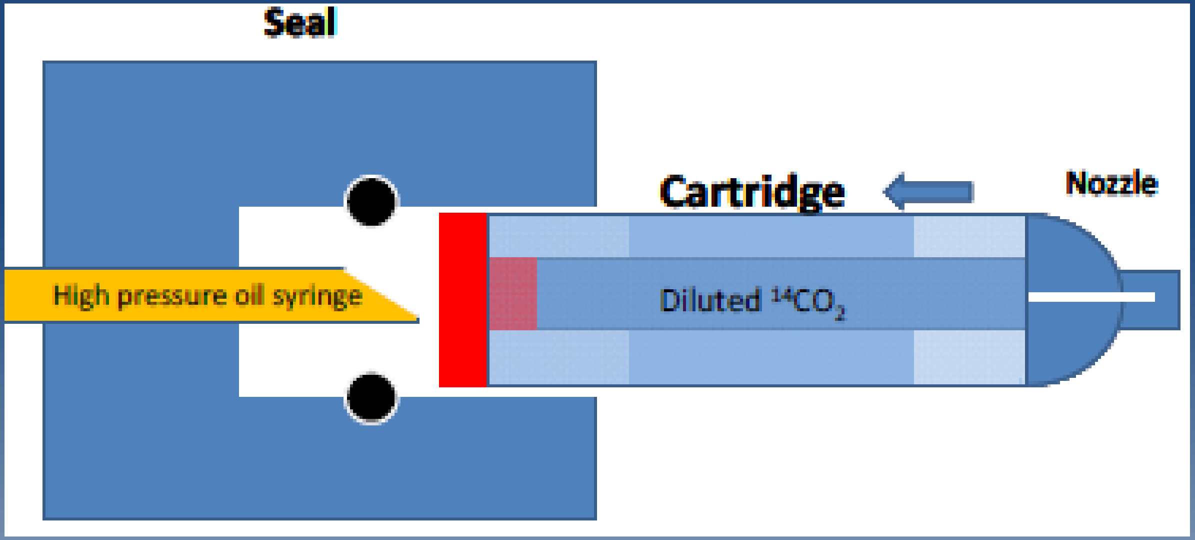
Filling Station
Pure $^{14}CO_2$(g)
Microcartridge
100 μg/day of compressed $^{14}CO_2$(g)
Syringe
100 μg/day of dissolved $^{14}CO_2$ in 10 mg solvent
CO_2(sc)
1 kg/s
1 ppt ^{14}C
CO_2 Detector

Microcartridge System



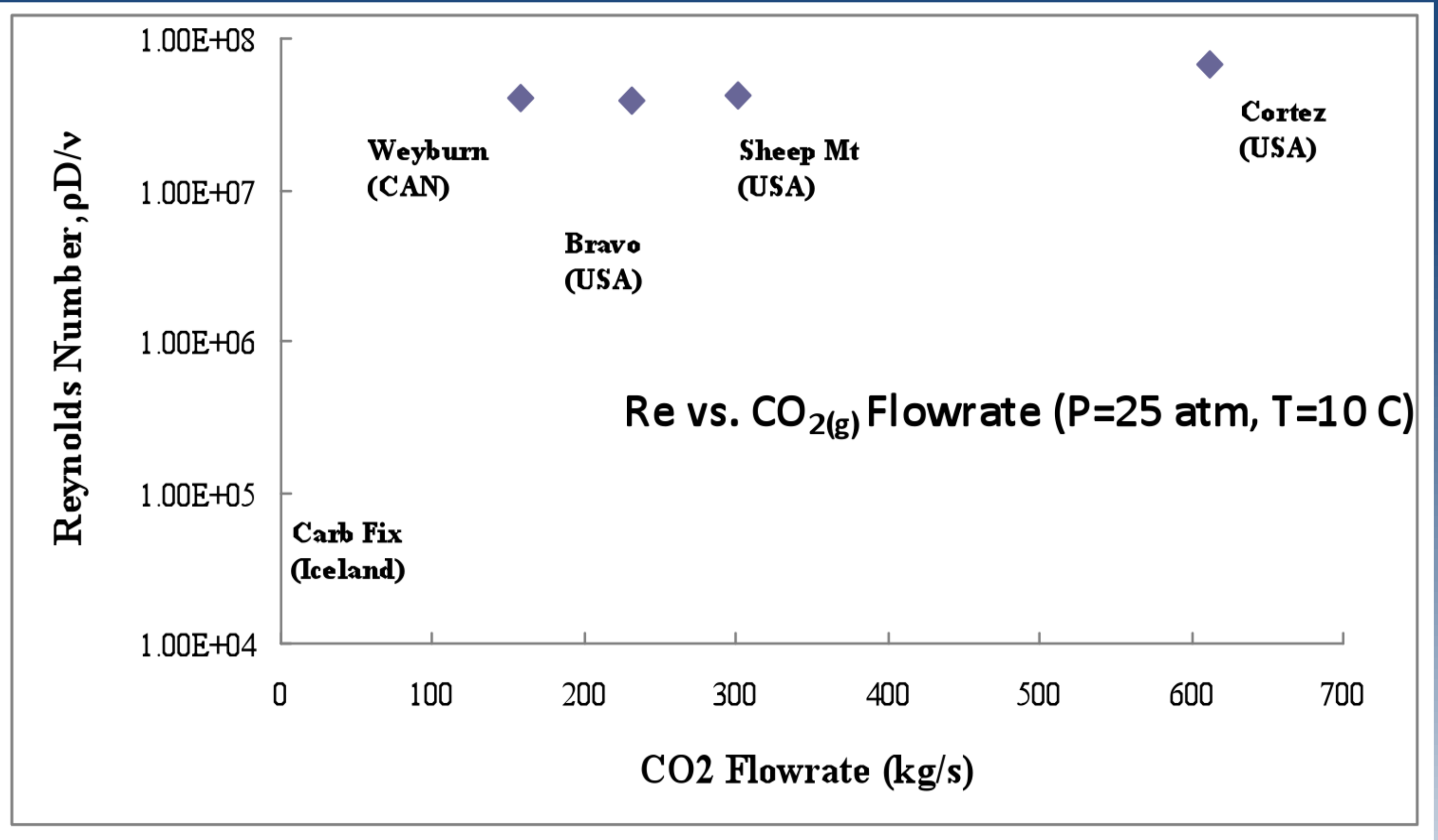
- Microfluidic chip design for pure $^{14}CO_2$ gas supply for 100,000 sec (~ 1 day)
- pressure reservoir with high viscosity fluid, activated by piezocrystal
- Delivers 1pg/s of $^{14}CO_2$ at 150 bars

Syringe System

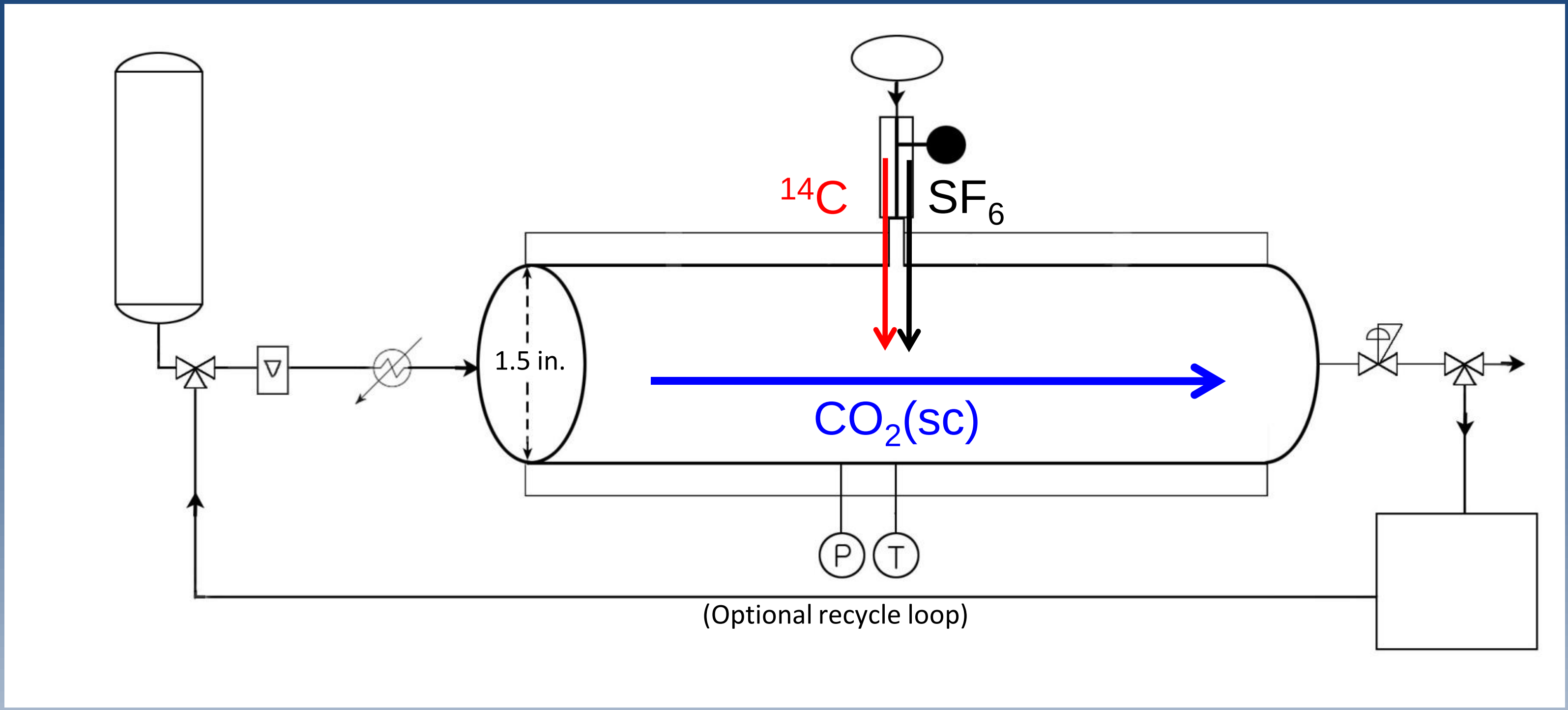


- Liquid supply system
- $^{14}CO_2$ dissolved in 10 microliters of fluid
- Delivers $^{14}CO_2$ at 150 bars

CO_2 Flow in Pipelines

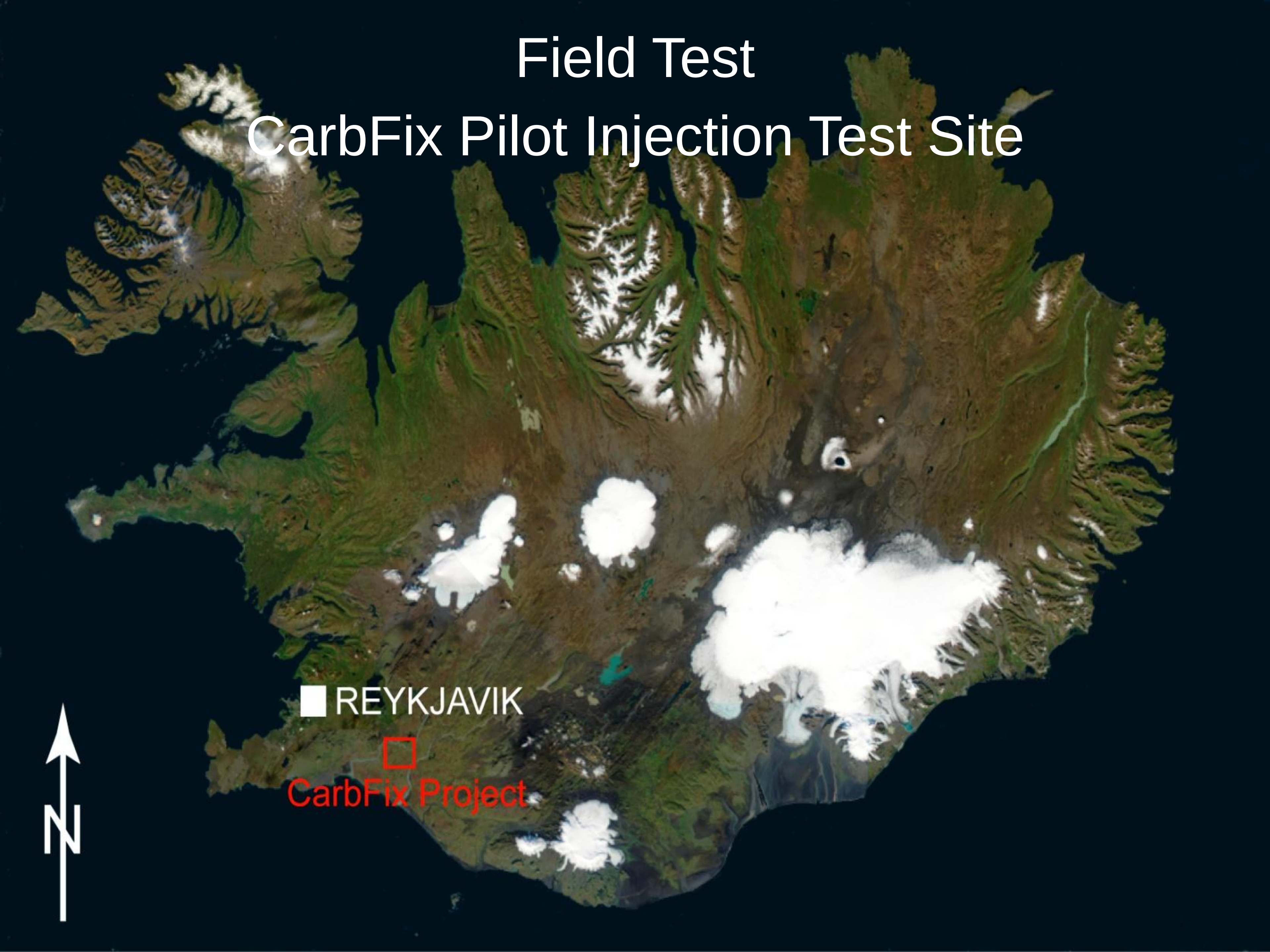


High Pressure Flow System For Mixing

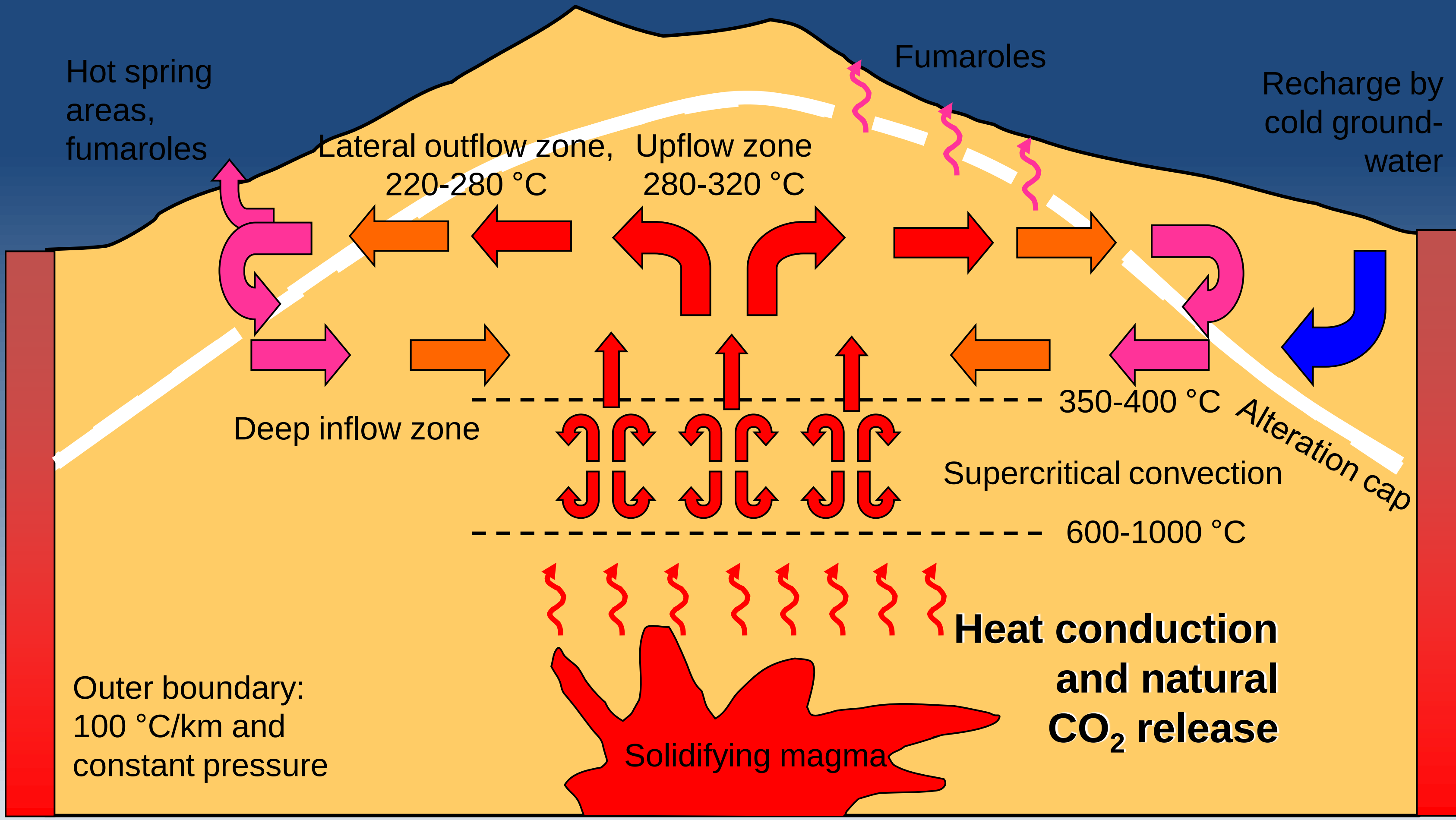


- Three fluid systems tested: water, liquid CO_2, and supercritical CO_2
- Unit mimics high pressure CO_2 transport to sequestration well
  - ✓ 1 kg/s CO_2 flow rate
  - ✓ Max Pressure = 150 atm

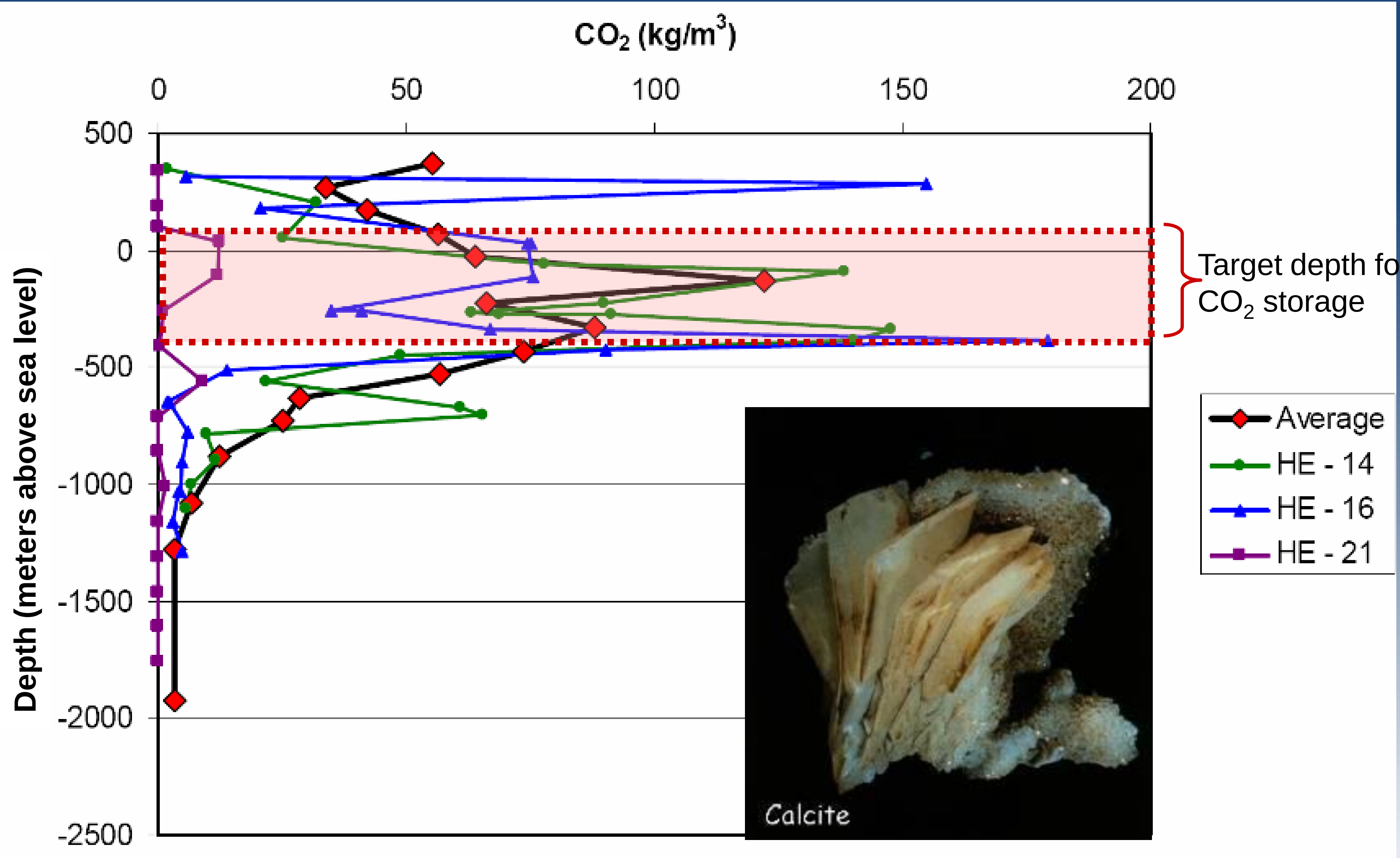
Field Test
CarbFix Pilot Injection Test Site



Magmatic CO_2 Source



Natural Mineral Carbonation in Iceland

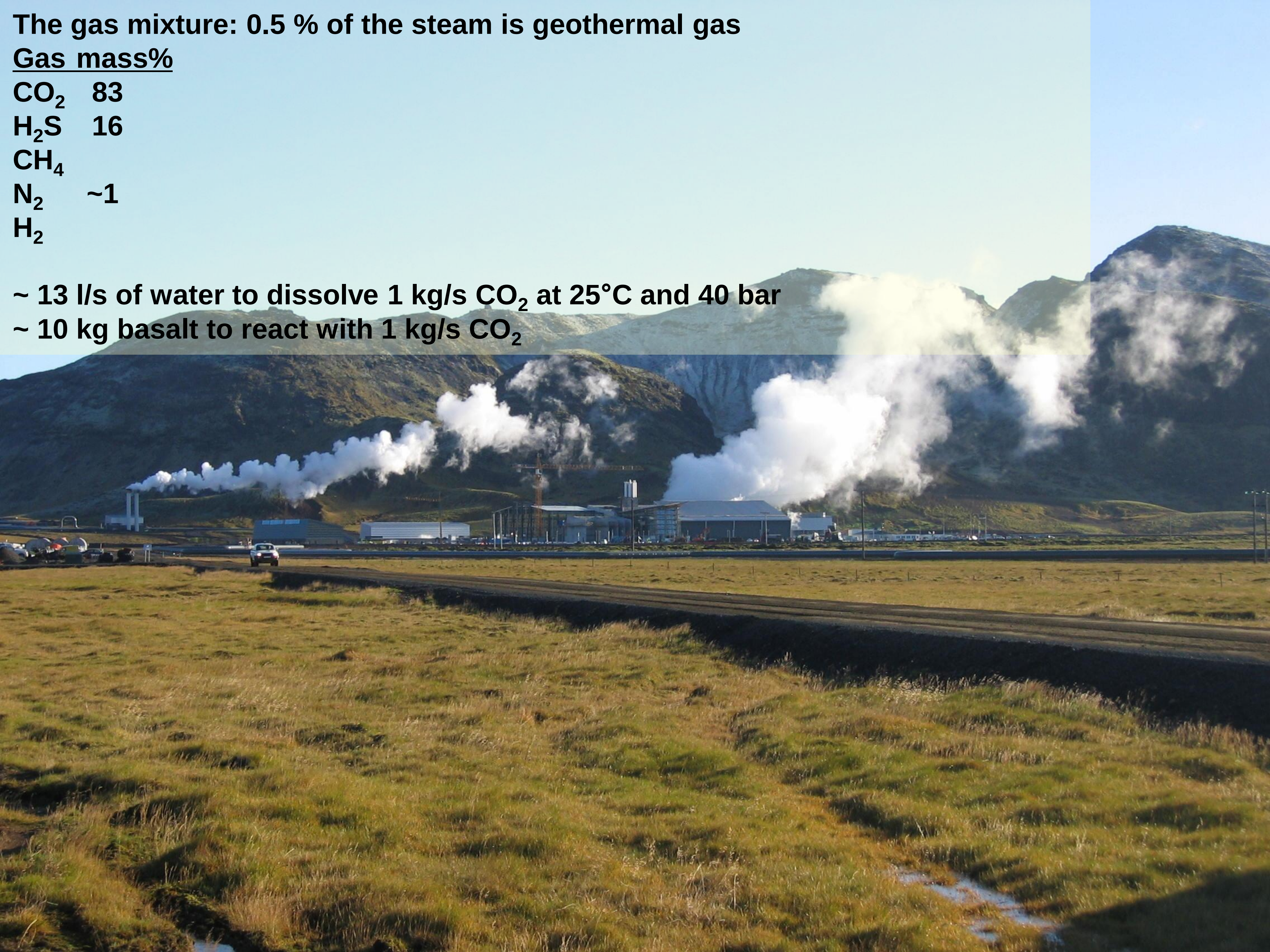


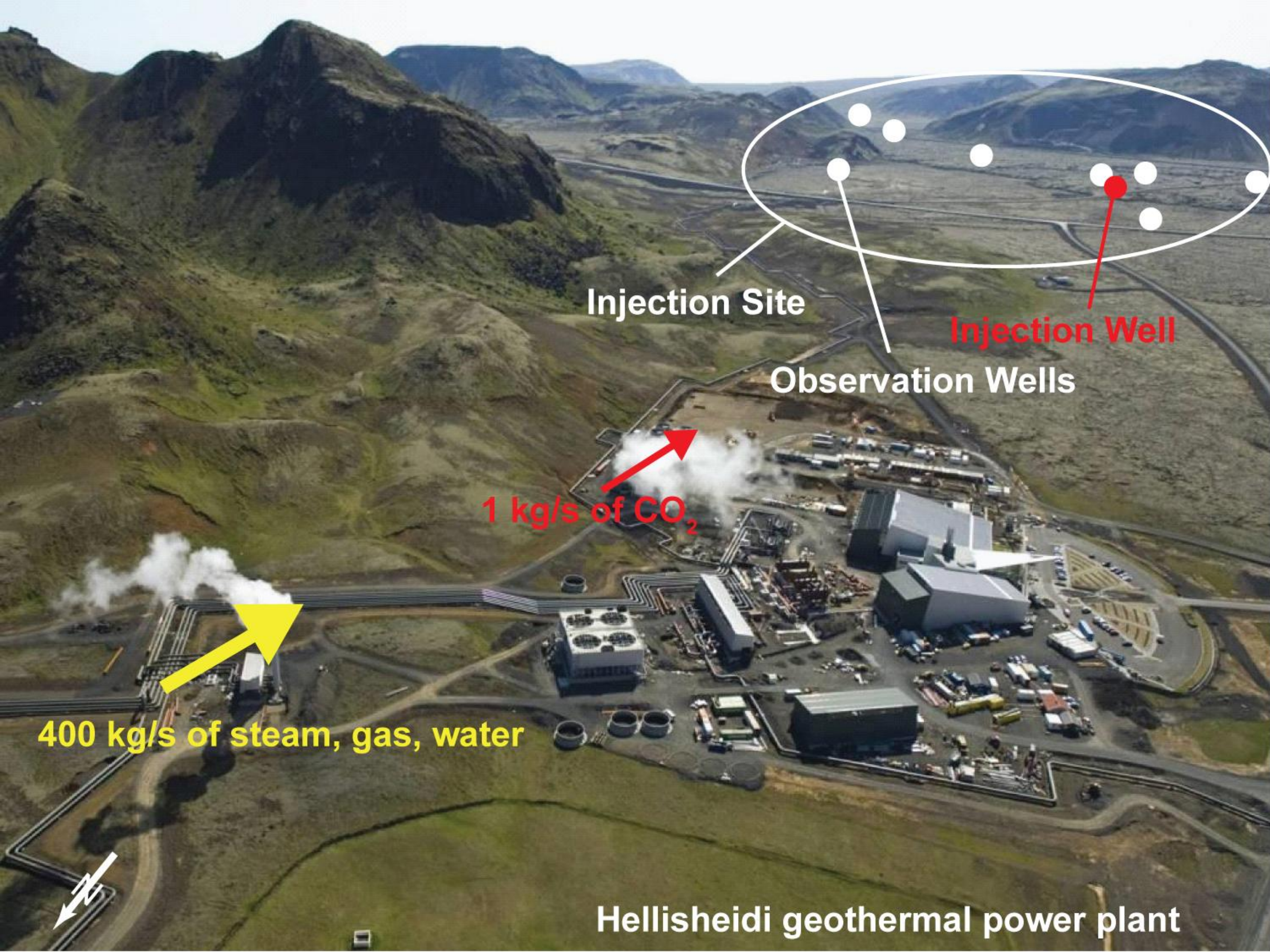
The gas mixture: 0.5 % of the steam is geothermal gas

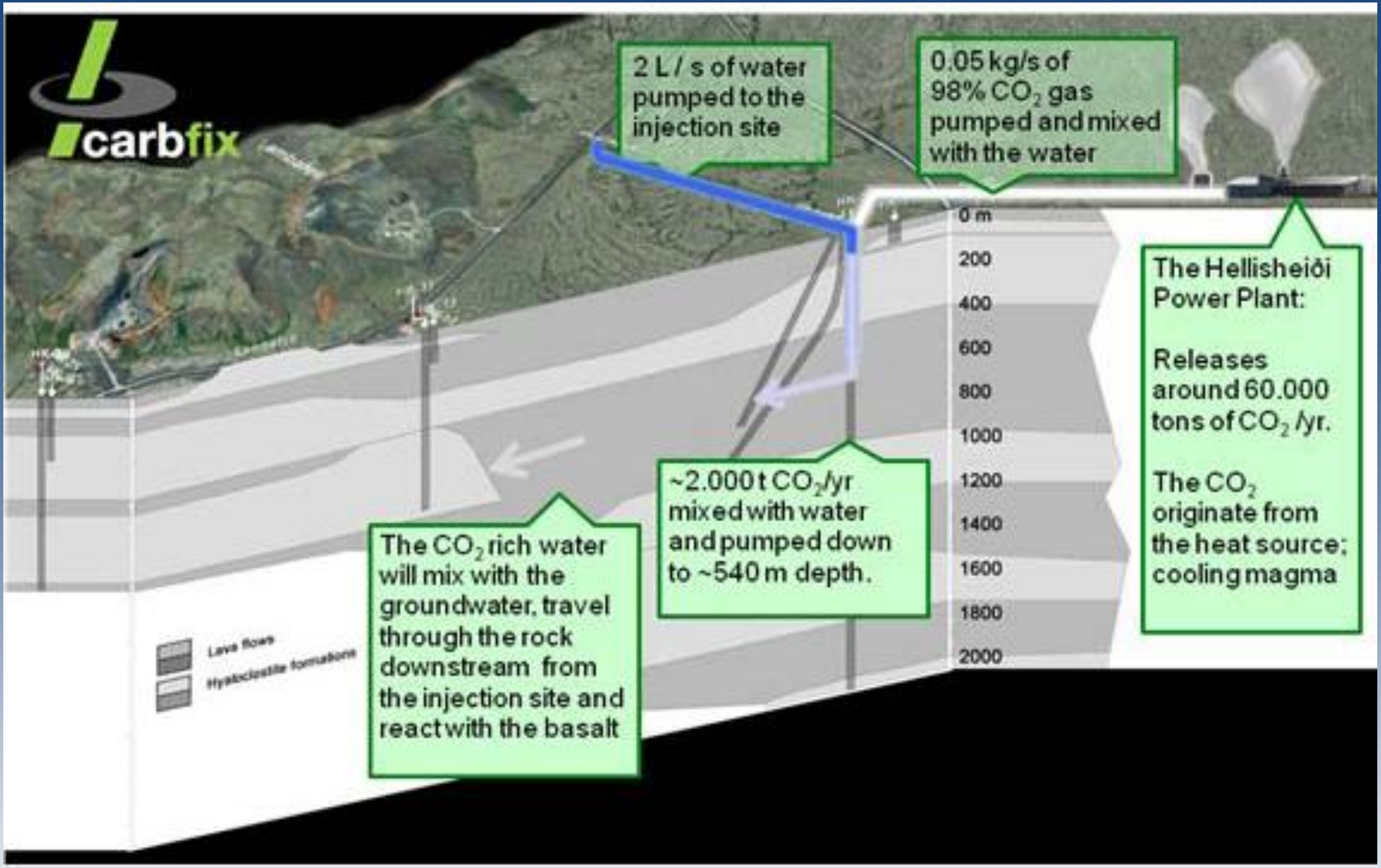
Gas	mass%
CO_2	83
H_2S	16
CH_4	
N_2	~1
H_2	

~ 13 l/s of water to dissolve 1 kg/s CO_2 at 25°C and 40 bar

~ 10 kg basalt to react with 1 kg/s CO_2

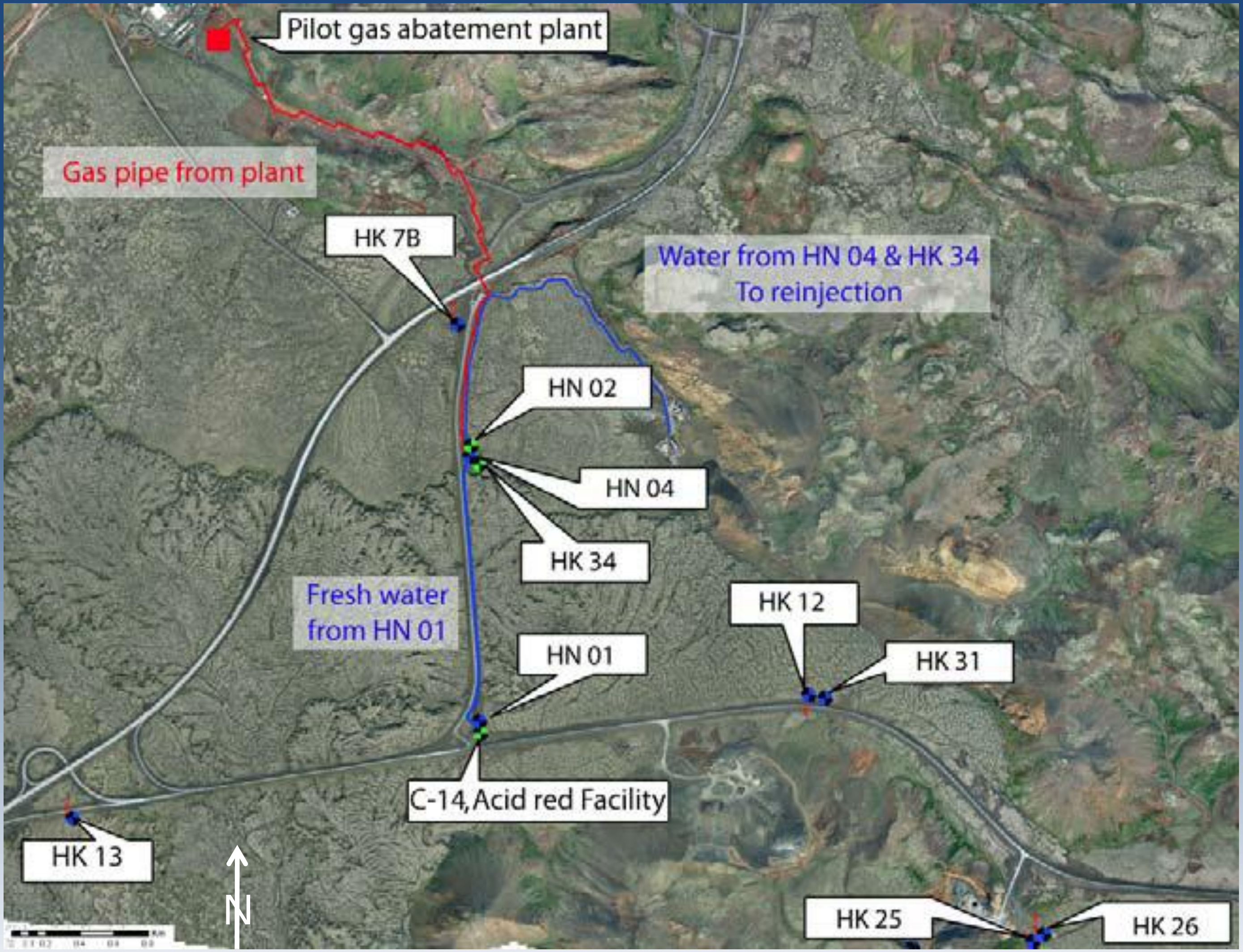



Injection Site
Injection Well
Observation Wells
1 kg/s of CO_2
400 kg/s of steam, gas, water
Hellisheidi geothermal power plant



carbfix
2 L / s of water pumped to the injection site
0.05 kg/s of 98% CO_2 gas pumped and mixed with the water
0 m
200
400
600
800
1000
1200
1400
1600
1800
2000
The Hellisheiði Power Plant:
Releases around 60.000 tons of CO_2 /yr.
The CO_2 originate from the heat source; cooling magma
~2.000 t CO_2/yr mixed with water and pumped down to ~540 m depth.
The CO_2 rich water will mix with the groundwater, travel through the rock downstream from the injection site and react with the basalt
Lava flows
Hyaloclastite formations

MVA Infrastructure



CO_2-Water-Rock Reactions

Dissolution of CO_2 and Dissociation

$$CO_2(g) \overset{K_h}{=} CO_2(aq)$$

$$CO_2(aq) + H_2O \overset{K_1}{=} HCO_3^{-} + \mathbf{H^+} \overset{K_2}{=} CO_2^{3-} + \mathbf{2H^+}$$

Mineral Dissolution

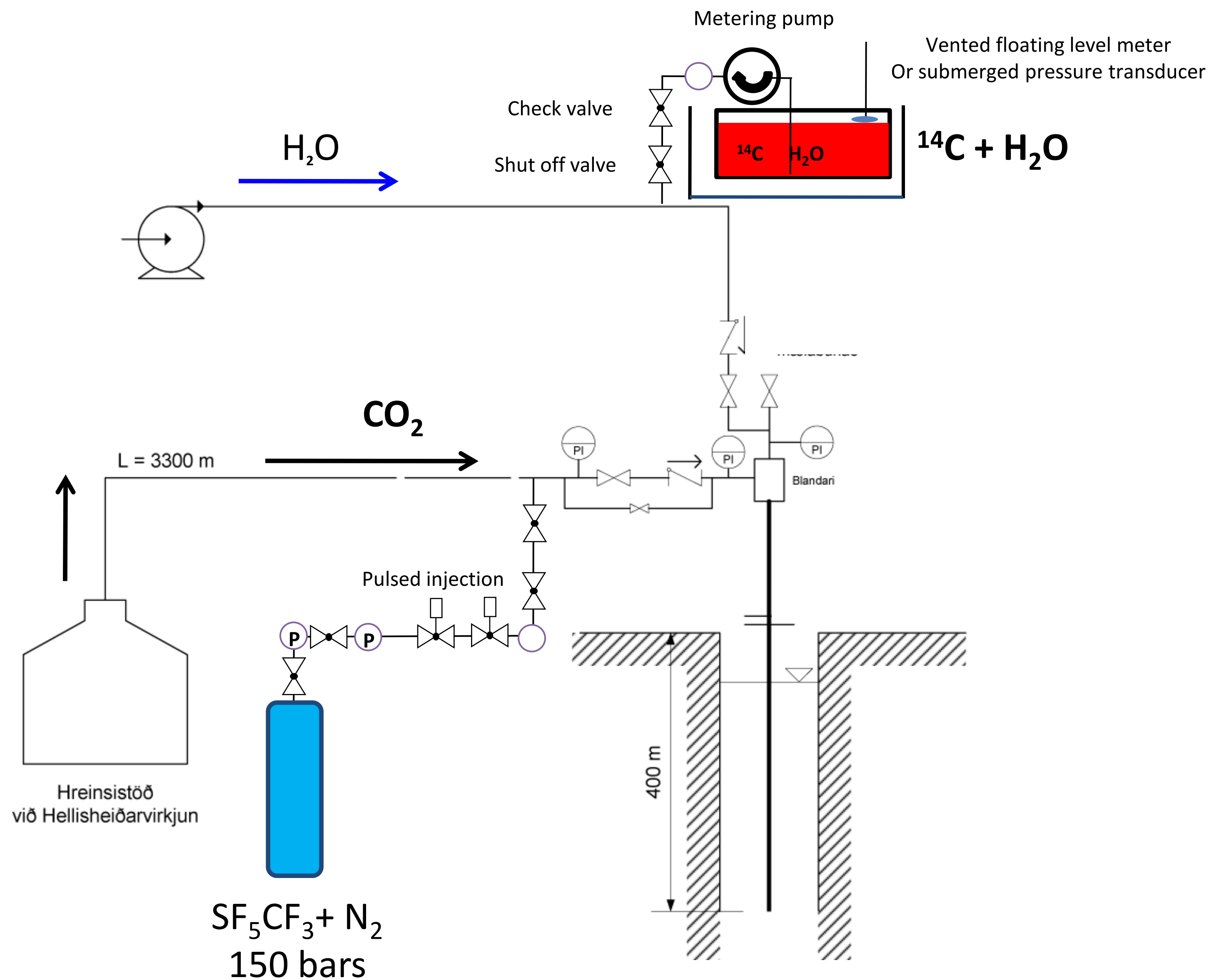
$$Mg_2SiO_4 + \mathbf{4H^+} \overset{k_1}{->} 2Mg^{2+} + SiO_2 + 2H_2O$$

$$CaAl_2Si_2O_8 + \mathbf{2H^+} + H_2O \overset{k_2}{->} Ca^{2+} + Al_2Si_2O_5(OH)_4$$

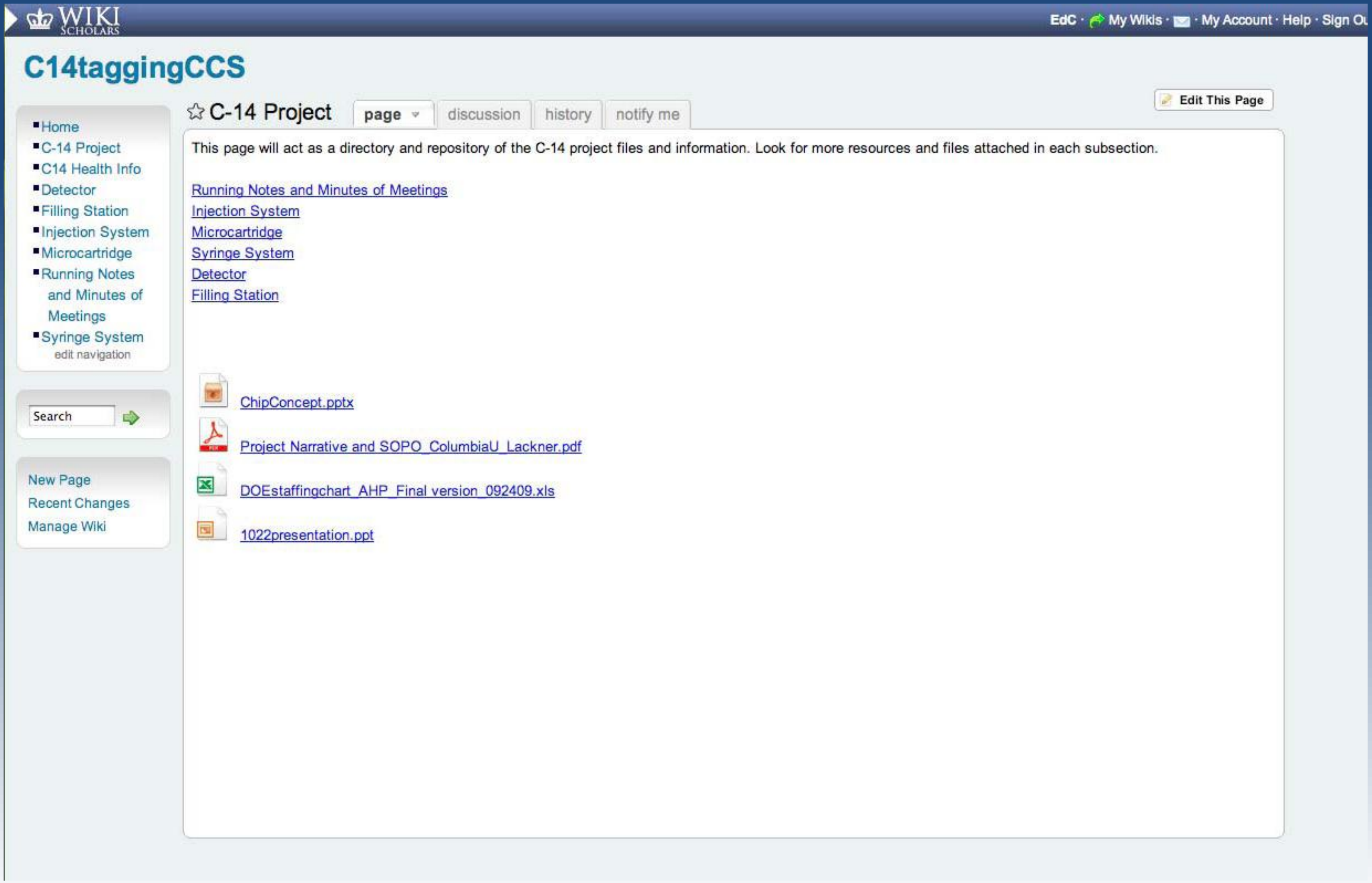
Mineral Precipitation

$$(Ca^{2+}, Mg^{2+}, Fe^{2+}) + CO_3^{2-} \overset{K_3}{=} (Ca, Mg, Fe)CO_3(s)$$

Monitoring & Accounting



Data Compilation and Reporting



Summary

- Tagging CO_2 with ^{14}C and counting it in the reservoir can establish a mass balance and inventory of anthropogenic CO_2 stored. ^{14}C counts are directly proportional to anthropogenic C in the reservoir.
- Allows monitoring of solubility and mineral trapping, plume tracking and leakage detection.
- Establish a strong correlation between different monitoring methods. ^{14}C method augments other monitoring technologies.
- Our ^{14}C MVA method requires well penetration and perforation and sampling apparatus.
- Method is labor intensive.